An In-Depth Study on the Mechanical and Thermal Properties of Nanoclay Reinforced Polymers at Various Temperatures

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Abstract

In this study, the mechanical properties of nanoclay reinforced polymeric resins are investigated at various temperatures. In recent years there has been heightened interest to develop nanoclay reinforced composites due to their superior performance compared to neat resins at high temperatures under various loading conditions, including impact. First, polypropylene (PP) resin specimens reinforced with varying weight fractions of nanoclay (0%, 1%, 3%, 6% and 10%) some instrumented with strain gages, were subjected to tensile loads and the stress-strain curves were obtained to determine the mechanical properties of the nanocomposite. Extensive experimental data were obtained. The results indicate that as the weight percentage of nanoclay increases, the strength and stiffness of the resulting nanocomposites also increase. Most of PP specimens exhibited significant deformation (more than 100%) and did not break. High temperatures have a deleterious effect on the strength and stiffness of nanoclay reinforced PP specimens. However, the addition of nanoclay, somewhat mitigates the deterioration of these properties. At lower temperatures the material stiffens, has higher strength and becomes more brittle as failure occurs at much lower strains. Also the tests using different PP resins indicate that the type of resin used has significant effect on the properties of the nanocomposite. A micromechanics model based on the Mori-Tanaka formulation was used to predict the results obtained experimentally. The comparison of theoretical/numerical and experimental results indicates that the Mori-Tanaka formulation may be a useful tool in predicting these properties.

I. Introduction

In recent years there has been heightened interest in developing nanoclay reinforced composites due to their improved performance at high temperatures under various loading conditions, including impact. It is believed that the reinforcement of polymeric resins with nanoclay may improve not only the strength and stiffness of the material, but also fire retardancy and smoke toxicity, thus providing better protection to personnel in civilian and military vehicles. The literature on nanoclay reinforced polymers is extensive. As examples, one may refer to [1-9], especially the excellent review by F. Hassain, et al. [9] on nanoparticle reinforced polymeric nanocomposites. The aim of this research project is to conduct a comprehensive study to determine the properties of nanoclay reinforced polymers under tensile loads, by varying the nanoclay reinforcement from 0% to 10% and the temperature from -54ºC (-65°F) to 71ºC (160°F) with the ultimate goal of using these properties in studying impact loading. To elicit the effect of resin, nanocomposites with three different resins were also tested under tensile loading. To predict the experimental results a micromechanics model based on the Mori-Tanaka formulation was used. The comparison of theoretical/numerical and experimental results indicates that the Mori-Tanaka formulation may be a useful tool in predicting these properties.

II. The Experimental Work

The tensile testing undertaken under this research has two distinct goals: a) to determine the effect of nanoclay reinforcement and temperature on the mechanical properties of nanoclay reinforced polymers and b) to use the obtained baseline data in impact analysis of the resulting composites. First, ASTM standard Type I dog-bone shaped polypropylene (PP) resin specimens reinforced with varying weight fractions of nanoclay (0%, 1%, 3%, 6% and 10%), some of which instrumented with strain gages, were subjected to tensile loads at room temperature and the stress-strain curves were obtained to determine the mechanical properties of the nanocomposite. Next the specimens were tested at various temperatures, from -54ºC (-65°F) to 71ºC (160°F) to elicit the effect of temperature. The effect of resin was also studied by using 3 different PP resins. For each data point at least 5 specimens were tested.

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Even though we have extensive experimental data, due to space limitation here we present only some representative results to depict our findings. The results obtained for the 5 specimens tested for each data point were remarkably consistent. Thus, in the figures typical test curves are used. Figure 1 shows the effect of increased nanoclay reinforcement on the mechanical properties of the resulting nanocomposite. As the weight percentage of nanoclay increases from 1% to 10% the ultimum stress and the stiffness of the material increase perceptibly. These increases can be more clearly observed from the results given in Table 1. It must be noted that PP based nanocomposites display significant deformation before failure (more than 100%).

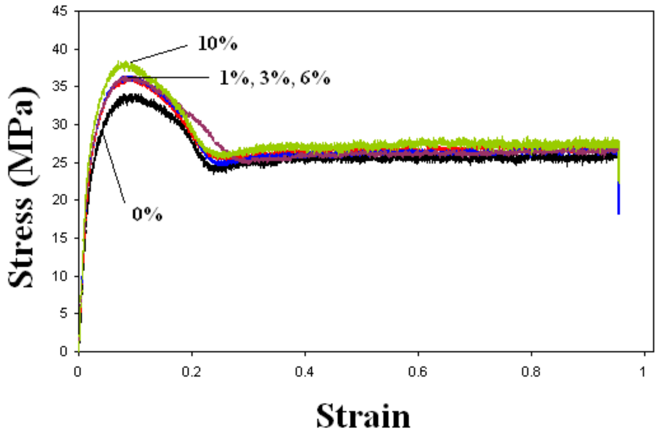

Figure 1. Effect of nanoclay reinforcement at room teperature

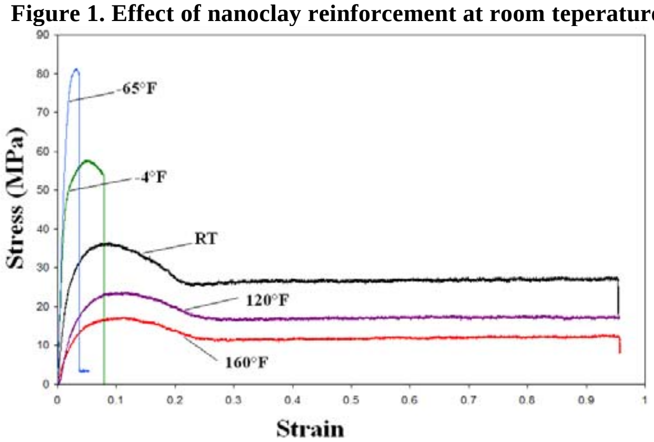

Figure 2. Effect of temperature on PP specimens reinforced with 1% nanoclay

Figure 2 depicts the effect of temperature on the properties of PP with 1% nanoclay reinforcement. It is first noted that at the higher temperatures the strength and stiffness are reduced significantly compared with those at room temperature. Whereas at lower temperatures the material stiffens, has higher strength and fails at relatively low strains.

Similar behaviour is also observed at higher percentages of nanoclay reinforcement. However, the deterioration of properties observed at higher temperatures is somewhat mitigated as the percentage of nanoclay increases. For example, as seen in Figure 3, at 49°C (120°F) an increase in the percentage of nanoclay reinforcement leads to higher stiffness and strength. One may note that while the addition of 1% nanoclay increases the stiffness and strength perceptibly, further nanoclay reinforcement does not contribute to significant improvement.

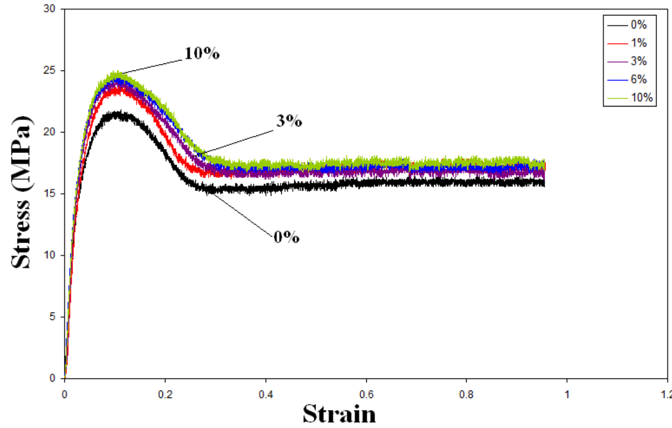

Figure 3. Effect of reinforcement at high temperature (120ºF)

Next specimens with three different PP formulations and the same 3% nanoclay reinforcement were subjected to tensile loading at room, high and low temperatures. The results for room temperature shown in Figure 4 indicate that the PP resin formulation may have drastic effects on the properties of the nanocomposite, especially failure elongation. For example, at room temperature TP 3868 fails at relatively low strains compared to Borealis and PP 3371 resins (Figure 4).

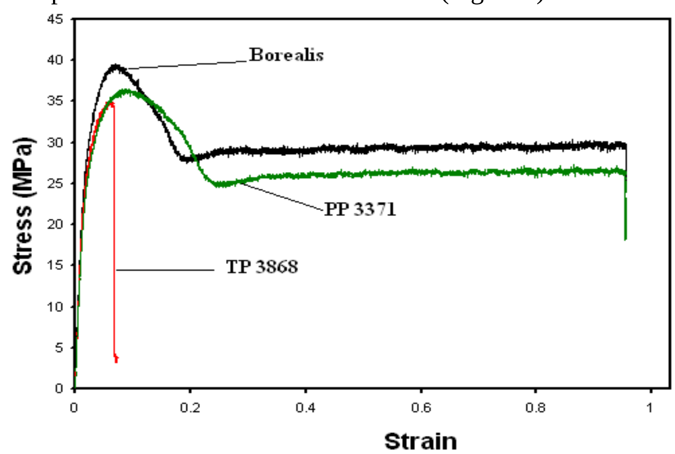

Figure 4. Effect of different resins with 3% nanoclay reinforcement

At higher temperatures (for example at 71°C) the behaviour of TP 3868 changes drastically, and its failure strain becomes comparable to that of Borealis and PP 3371 resins (Figure 5). At lower temperatures, all three resins have similar behaviour (Figure 6). However, TP 3868 fails first, while PP 3371 resin has the highest failure strain.

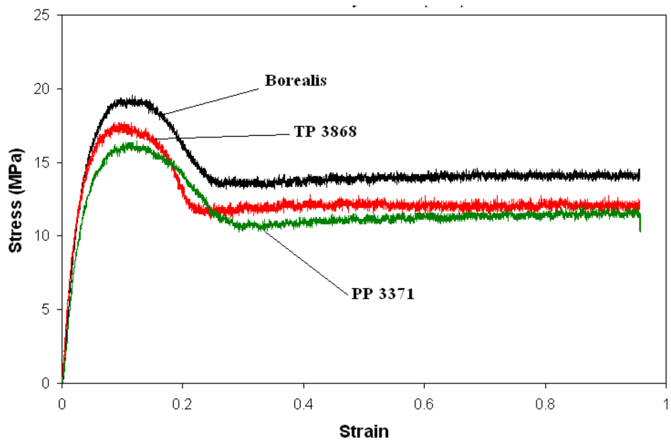

Figure 5. Stress-strain curves of PP 3371, Borealis and TP 3868 resins with 3% nanoclay reinforcement at 71°C (160°F)

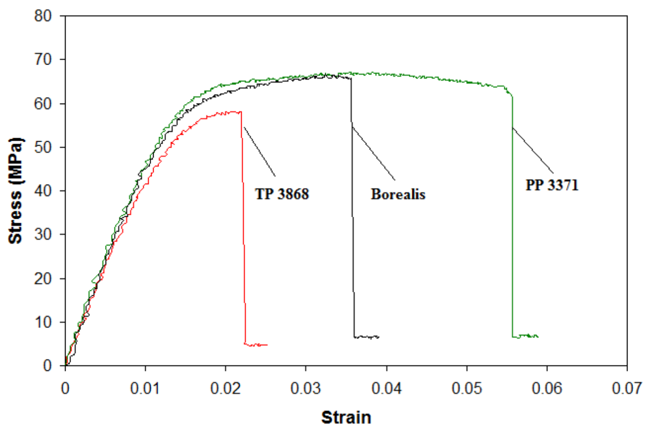

Figure 6. Stress-strain curves of PP 3371, Borealis and TP 3868 resisn with 3% nanoclay reinforcement at -20°C (-4°F)

Some of the results for nanoclay reinforced PP specimens are also summarized in Table 1. The results indicate that with increasing nanoclay reinforcement the Young's Modulus and ultimate stress increase perceptibly as noted previously. As discussed previously temperature also has significant effect on the nanocomposite properties.

Table 1. Properties obtained experimentally for nanoclay reinforced PP specimens

Temperature	Nanoclay Reinforced	E_1 (GPa)	Ult. Stress (MPa)	Strain at Ult. Stress	Necking Stress (MPa)	End of Test Strain*
Room Temperature	0%	1.285	33.044	0.098	24.805	0.954
	1%	1.489	35.346	0.091	26.071	0.954
	3%	1.557	35.096	0.094	25.392	0.953
	6%	1.616	35.590	0.092	25.751	0.954
	10%	1.809	36.584	0.089	26.160	0.953
120°F (49°C)	0%	0.743	21.678	0.105	15.330	0.956
	1%	0.748	23.209	0.108	16.613	0954
	3%	0.811	23.952	0.108	16.793	0.954
	6%	0.857	24.537	0.108	17.040	0.953
	10%	0.878	24.717	0.110	17.041	0.955
160°F (71°C)	0%	0.403	14.542	0.130	10.378	0.957
	1%	0.499	15.803	0.121	11.188	0.957
	3%	0.480	16.141	0.117	11.210	0.957
	6%	0.519	16.433	0.113	11.143	0.955
	10%	0.531	16.883	0.110	11.413	0.954
-20°C (-4°F)	0%	4.077	55.715	0.055	43.500	0.103
	1%	4.541	57.719	0.046	50.280	0.070
	3%	5.152	67.648	0.038	62.379	0.055
	6%	5.219	67.961	0.039	60.915	0.065
	10%	5.234	68.156	0.034	63.639	0.048
-54°C (-65°F)	0%	4.720	78.136	0.032	70.798	0.053
	1%	5.328	81.459	0.032	79.786	0.038
	3%	5.322	83.337	0.024	81.176	0.028
	6%	5.297	81.513	0.025	80.185	0.028
	10%	5.660	80.703	0.023	80.365	0.023

* End of test strain may indicate failure strain (in case of failure) or strain when test was ended.

III. Modeling and Numerical Results

To predict the properties obtained experimentally, the Young's modulus was calculated using the Mori-Tanaka Model [10]. The Mori-Tanaka Model is based on micromechanics and uses Eshelby's solution for inclusions embedded in an infinite matrix. Here we approximate the nanoclay flakes as thin disks with the aspect ratio α calculated as the thickness to length ratio. Referring to [10], the normalized Young's modulus of the nanocomposite can be expressed as:

$$\frac{E_1}{E_m} = \frac{1}{1 + c(A_1 + 2\nu_m A_2)A}$$

where, E_1 and E_m are the Young's moduli of the composite and the matrix respectively, c is the volume fraction of nanoclay and the coefficients A_1, A_2 and A are given by:

$$A_1 = D_1(B_4 + B_5) - 2B_2$$

$$A_2 = (1 + D_1)B_2 - (B_4 + B_5)$$

and

$$A = 2B_2B_3 - B_1(B_4 + B_5)$$

where

$$B_1 = cD_1 + D_2 + (1-c)(D_1S_{1111} + 2S_{2211})$$

$$B_2 = c + D_3 + (1-c)(D_1S_{1122} + S_{2222} + S_{2233})$$

$$B_4 = cD_1 + D_2 + (1-c)(S_{1122} + D_1S_{2222} + S_{2233})$$

$$B_5 = c + D_3 + (1-c)(S_{1122} + S_{2222} + D_1S_{2233})$$

and

$$D_1 = 1 + 2(\mu_p - \mu_m)/(\lambda_p - \lambda_m)$$

$$D_2 = (\lambda_m + 2\mu_m)/(\lambda_p - \lambda_m)$$

$$D_3 = \lambda_m / (\lambda_p - \lambda_m)$$

The *D* terms are defined by using μ_m, λ_m and μ_p, λ_p, which are the Lamé constants of the matrix and inclusions, respectively. In the *B* terms, the components of Eshelby's tensor S_{ijkl} given below are used:

$$S_{1111} = \frac{1}{2(1-\nu_m)}\{1 - 2\nu_m + \frac{3\alpha^2 - 1}{\alpha^2 - 1} - [1 - 2\nu_m + \frac{3\alpha^2}{\alpha^2 - 1}]g\}$$

$$S_{2222} = S_{3333} = \frac{3}{8(1-\nu_m)}\frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4(1-\nu_m)}[1 - 2\nu_m - \frac{9}{4(\alpha^2 - 1)}]g$$

$$S_{2233} = S_{3322} = \frac{1}{4(1-\nu_m)}\{\frac{\alpha^2}{2(\alpha^2 - 1)} - [1 - 2\nu_m + \frac{3}{4(\alpha^2 - 1)}]g\}$$

$$S_{2211} = S_{3311} = -\frac{1}{2(1-\nu_m)}\frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4(1-\nu_m)}\{\frac{3\alpha^2}{\alpha^2 - 1} - (1 - 2\nu_m)\}g$$

$$S_{1122} = S_{1133} = -\frac{1}{2(1-\nu_m)}[1 - 2\nu_m + \frac{1}{\alpha^2 - 1}] + \frac{1}{2(1-\nu_m)}[1 - 2\nu_m + \frac{3}{2(\alpha^2 - 1)}]g$$

$$S_{2323} = S_{3232} = \frac{1}{4(1-\nu_m)}\{\frac{\alpha^2}{2(\alpha^2 - 1)} + [1 - 2\nu_m - \frac{3}{4(\alpha^2 - 1)}]g\}$$

$$S_{1212} = S_{1313} = \frac{1}{4(1-\nu_m)}\{1 - 2\nu_m - \frac{\alpha^2 + 1}{\alpha^2 - 1} - \frac{1}{2}[1 - 2\nu_m - \frac{3(\alpha^2 + 1)}{\alpha^2 - 1}]g\}$$

Here ν_m is the Poisson's ratio of the matrix. In Eshelby's tensor, the *g* term has two different expressions depending on the aspect ratio α of the inclusions:

$$g = \frac{\alpha}{\left(\alpha^2 - 1\right)^{3/2}}\left\{\alpha\left(\alpha^2 - 1\right)^{1/2} - \cosh^{-1}\alpha\right\};\ \alpha > 1$$

$$g' = \frac{\alpha}{\left(1 - \alpha^2\right)^{3/2}}\left\{\cos^{-1}\alpha - \alpha\left(1 - \alpha^2\right)^{1/2}\right\};\ \alpha < 1$$

In the calculations, for the matrix and the nanoclay the following material and geometric properties as shown in Tables 2 and 3 are used:

Table 2. Matrix properties at various temperatures

Properties / Temperature	E_m (GPa)	ν_m	γ_m (N/m^3)	μ_m (GPa)	λ_m (GPa)
-54ºC	4.720	0.35	8829	1.75	4.08
-20ºC	4.077	0.35	8829	1.51	3.52
RT	1.285	0.35	8829	0.48	1.11
49ºC	0.743	0.35	8829	0.28	0.64
71ºC	0.403	0.35	8829	0.15	0.35

Table 3. Properties of Nanoclay

	E_p (GPa)	ν_p	γ_p (N/m^3)	μ_p (GPa)	λ_p (GPa)
Properties	200	0.2	18639	83.33	55.56

It is assumed that the nanoclay properties do not change significantly in the temperature range considered in this study. Here for E_m we use the values obtained experimentally, for ν_m, ν_p and E_p we use typical values reported in the literature [8] and μ_m, μ_p, λ_m and λ_p are calculated.

First, we calculate the volume fraction of nanoclay to be able to use the Mori-Tanaka formulation. The volume fraction of nanoclay in terms of the weight fraction can be written as:

$$c = V_p = \frac{W_p / \gamma_p}{W_p / \gamma_p + \left(1 - W_p\right) / \gamma_m}$$

For each percentage of nanoclay reinforcement, the volume fraction of nanoclay is given in Table 4:

Table 4. Conversion of weight fractions of nanoclay to volume fractions

Weight fraction of nanoclay	Volume fraction of nanoclay
1 %	0.48 %
3 %	1.44 %
6 %	2.93 %
10 %	5 %

The thickness of the nanoclay particles depends on whether exfoliation has been achieved. In that case for an exfoliated nanoclay flake one may use d_s=0.615 nm, as a typical value used in literature [8]. However, in most likelihood, some nanoclay particles will be exfoliated and some will still have several layers. Here we assume that on average nanoclay particles will have three layers, thus d_s=3x0.615nm =1.845nm. For the diameter we use a typical value of a=200 nm [8]. Thus, the aspect ratio of nanoclay can be calculated as: $\alpha = d_s/a$ =0.009225. Since the aspect ratio of nanoclay is smaller than 1, we use g' in Eshelby's tensor. The calculations for various weight fractions (converted to volume fractions) were performed using commercial software. Comparison of the theoretical predictions and experimental results for the E_1/E_m ratio at various temperatures is shown in Figures 7-11. At the higher and lower temperatures the Young's modulus for matrix was obtained experimentally while the Young's modulus of nanoclay is assumed constant in the temperature range considered. The results indicate that there is good agreement between the experimental and theoretical results and thus the Mori-Tanaka formulation can be a useful tool in predicting the Young's modulus of the nanocomposite.

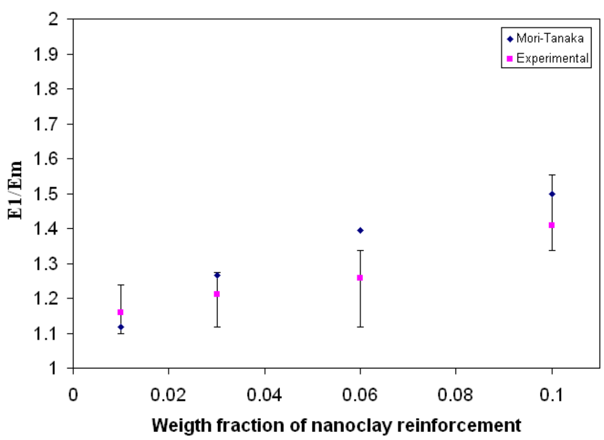

Figure 7. Comparison of Mori-Tanaka end experimental results at room temperature for nanoclay reinforced PP

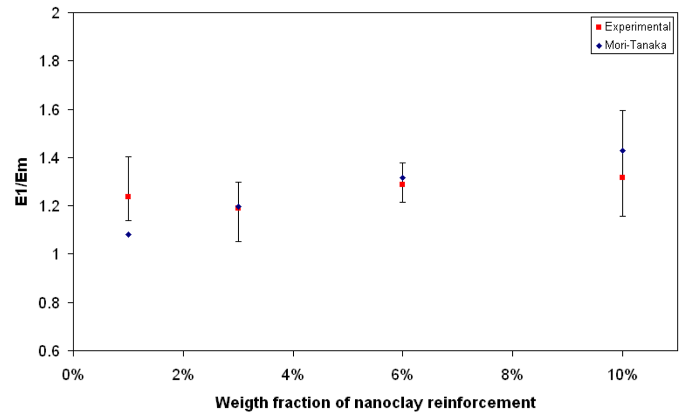

Figure 8. Comparison of Mori-Tanaka end experimental results at 71ºC (160ºF) for nanoclay reinforced PP

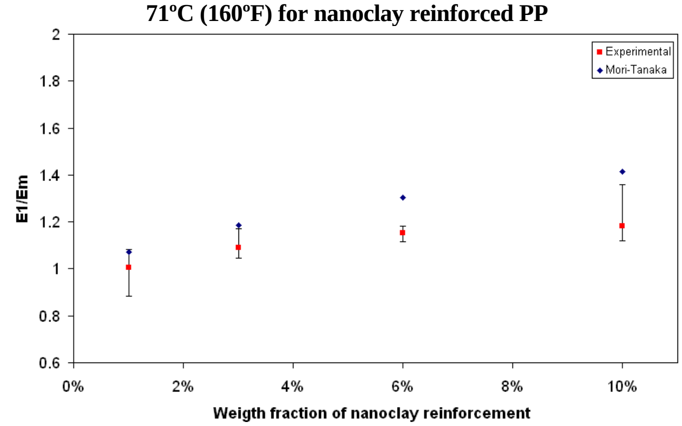

Figure 9. Comparison of Mori-Tanaka end experimental results at 49ºC (120ºF) for nanoclay reinforced PP

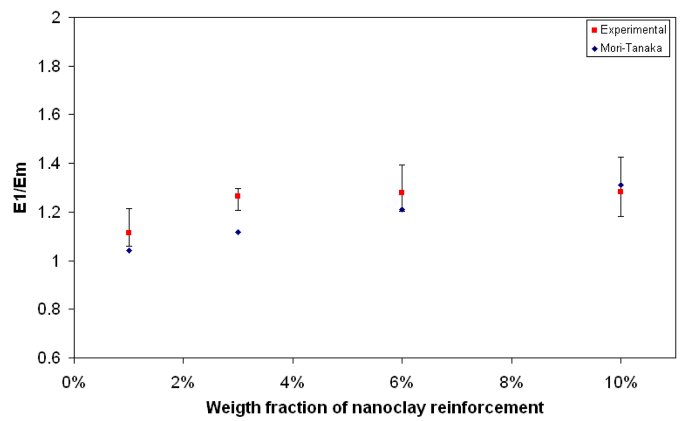

Figure 10. Comparison of Mori-Tanaka end experimental results at -20ºC (-4ºF) for nanoclay reinforced PP

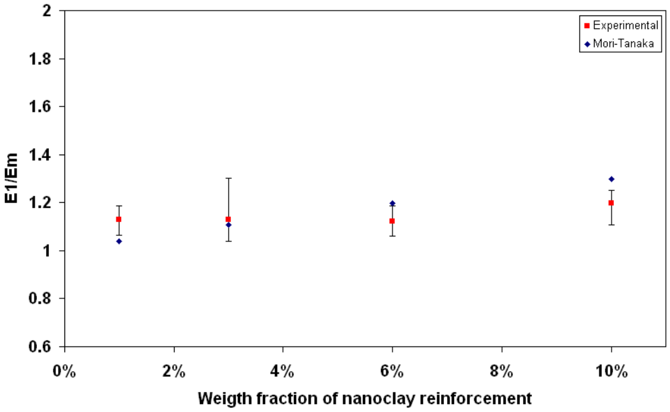

Figure 11. Comparison of Mori-Tanaka end experimental results at -54ºC (-65ºF) for nanoclay reinforced PP

IV. Conclusions

In this study the mechanical properties of three PP resins reinforced with nanoclay particles were studied at room, elevated and low temperatures. From the results obtained so far, the following conclusions can be deduced:

1. Nanoclay reinforcement improves the mechanical properties of PP resins. The strength and stiffness of the resulting nanocomposite increase as the percentage of nanoclay reinforcement increases
2. The choice of the PP resin can have a significant effect on the behavior of the nanocomposite, especially the failure strain
3. At higher temperatures the mechanical properties of PP deteriorate. However, the addition of nanoclay somewhat mitigates this deterioration
4. At low temperatures, the material stiffens, has higher ultimate stress and fails at comparatively low strains
5. The Mori-Tanaka formulation may be a useful tool in predicting the Young's modulus of the nanocomposite.

Acknowledgments

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